

50832 / 01

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
20 September 2001 (20.09.2001)

PCT

(10) International Publication Number  
**WO 01/68547 A1**

(51) International Patent Classification<sup>7</sup>: **C04B 14/14**,  
18/08, 38/08, 28/04

(21) International Application Number: **PCT/US01/07948**

(22) International Filing Date: **9 March 2001 (09.03.2001)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:  
60/189,235 14 March 2000 (14.03.2000) US  
09/803,456 9 March 2001 (09.03.2001) US

(71) Applicant (for all designated States except US): **JAMES HARDIE RESEARCH PTY LIMITED [AU/AU]**; 2nd floor, 1 Grand Avenue, Camellia, NSW 2142 (AU).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **GLEESON, James,**

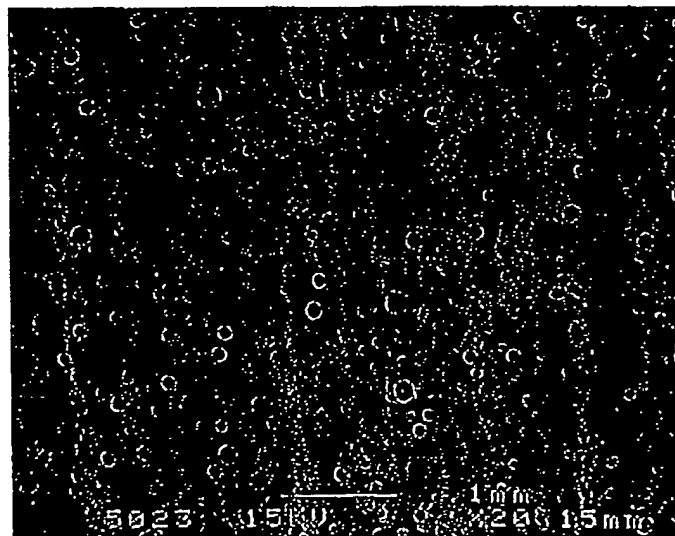
A. [AU/US]; 1169 Coronado Street, Upland, CA 91786 (US). **PARADIS, Kalyne, H.** [US/US]; 14090 Baldwin Court, Rancho Cucamonga, CA 91739 (US). **SLOANE, Brian, P.** [AU/AU]; 14 Nottingham Street, Old Toongabbie, NSW 2146 (AU). **MELMETH, David, L.** [AU/US]; 1919 Glenwood Way, Upland, CA 91784 (US). **SELIGMAN, Dean, M.** [US/US]; P.O. Box 2878, Mission Viejo, CA 92690 (US).

(74) Agent: **ALTMAN, Daniel, E.**; Knobbe, Martens, Olson and Bear, LLP, 620 Newport Center Drive, 16th Floor, Newport Beach, CA 92660 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, CZ (utility model), DE, DE (utility model), DK, DK (utility model), DM, DZ, EE, ES, FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

[Continued on next page]

(54) Title: **FIBER CEMENT BUILDING MATERIALS WITH LOW DENSITY ADDITIVES**



Pending

WO 01/68547 A1

(57) Abstract: This invention relates to a formulation with the addition of low density additives of volcanic ash, hollow ceramic microspheres or a combination of microspheres and volcanic ash or other low density additives into cementitious cellulose fiber reinforced building materials. This formulation is advantageously lightweight or low density compared as compared to current fiber cement products without the increased moisture expansion and freeze-thaw degradation usually associated with the addition of lightweight inorganic materials to fiber cement mixes. The low density additives also give the material improved thermal dimensional stability.



(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW). Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM). European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR). OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— with international search report

— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

## FIBER CEMENT BUILDING MATERIALS WITH LOW DENSITY ADDITIVES

### Background of the Invention

#### 5 Field of the Invention

This invention relates to building materials and methods for making the same, and more particularly to the addition of low density additives (LDA) into cementitious cellulose fiber-reinforced building materials.

#### Description of the Related Art

10 Fiber-reinforced cement (FRC) products such as water-resistant building sheets have been used for building since 1895. In recent history reinforcing fibers used in such products have included not only asbestos fibers, but also cellulose fibers (see Australian Patent No. 515151), metal fibers, glass fibers and other natural and synthetic fibers. Typically, the density of such building sheets is from about 1.2-1.7 g/cm<sup>3</sup>, the variation in density typically being achievable by compression and dewatering of the fiber cement slurries used in manufacture and by varying the amount of fiber used. At these densities, the cement based matrix has few voids, which results in lower water absorption  
15 which has usually been considered necessary for good durability performance of cement matrices.

The densities of fiber cement described above mean the products are heavier than timber based products of equal dimension and have reduced workability. Workability encompasses the ease with which the board is handled and installed. Therefore, fiber cement building products are more difficult to cut, machine and nail than timber and timber based products. In this regard, the density of natural timber sheets typically ranges from about 0.7-0.9 g/cm<sup>3</sup> for dry  
20 hardwoods and from about 0.38-0.6 g/cm<sup>3</sup> for dry softwoods. Thus, a density-modified fiber cement material with density similar to timber may be expected to improve workability and enable lighter, more nailable, easier to cut and easier to machine products to be manufactured. However, this would have to be achieved while retaining the durability, fire resistant, rot proof and water resistant properties of fiber cement if the density modified fiber cement is to be used in the same range of applications.

25 Prior art describes how lightweight inorganic powders can be added as density modifiers in cement or fiber-reinforced cement materials. Low density additives for FRC products are defined as having a loose bulk density of about 0.8 g/cm<sup>3</sup> (about 50 lbs./cu.ft.) or less. The typical low density additives (LDA) used include low bulk density calcium silicate hydrates (CSH), expanded polystyrene beads (EPS), expanded vermiculite, expanded perlite, expanded shale, and expanded clay. The density modification of cement-based materials with such inorganic particles is  
30 primarily achieved by introducing porosity into the material. Typically, the pore spaces are filled with water when the material is submerged in water or exposed to rain for a length of time. This causes these materials to have poorer wet to dry dimensional stability (moisture resistance), a higher saturated mass, and poor freeze-thaw resistance.

Accordingly, there is a need for a lightweight FRC building material and method for manufacturing the same with improved wet to dry dimensional stability over that of typical density modified products. Secondly, the  
35 lightweight building material should maintain similar wet to dry dimensional stability as that of FRC products without

density modifiers if the density modified material is to be used in the same range of applications. In addition, it is highly preferred in some applications that the material also have a low saturated mass, good freeze-thaw resistance, and high temperature dimensional stability. Finally, it is also desirable to have a FRC building product where lower ranges of densities closer to that of timber and timber based products can be achieved with improved durability.

#### Summary of the Invention

Two low density additives have been evaluated that have properties more desirable to FRC building materials than typical low density additives. These two low density additives are volcanic ash and hollow ceramic microspheres. One embodiment of the invention includes the addition of volcanic ash (VA) into an FRC building material. A second embodiment comprises the addition of hollow ceramic microspheres (microspheres) into the FRC building material. A third embodiment incorporates the blending of microspheres with volcanic ash and/or other typical low density additives into the FRC building material. The third embodiment with the blend of microspheres and VA and/or other low density additives may be more preferable than the first embodiment with the introduction of volcanic ash by itself. The second embodiment with the addition of microspheres by themselves may be more preferable than either the first or third embodiments as described above, depending on the properties being considered for a particular application.

Compared to current FRC products, one advantage of the first embodiment with volcanic ash is that it provides the product with low densities and improved workability at an economical price, as well as improved dimensional stability over that of typical low density additives.

The second embodiment encompasses the addition of microspheres in fiber-cement products. Compared to current FRC products, the benefits of adding microspheres include the low density and improved workability of the product without increased moisture expansion or freeze-thaw degradation associated with the addition of lightweight inorganic materials to FRC mixes. Moreover, the addition of microspheres provides improved thermal dimensional stability for FRC material.

The third embodiment relates to the addition of microspheres in combination with VA and/or other typical low density additives in FRC material. Blending microspheres with other low density additives is advantageous because lower density FRC products can be achieved with less weight percent addition (as compared to microspheres only) due to the lower densities of VA and other typical LDA relative to microspheres. This also enables fiber cement products to achieve lower density ranges to further improve workability, while microspheres minimize the adverse effects typical low density additives have on wet-to-dry dimensional stability and overall durability.

Thus, in one aspect of the present invention, a building material is provided comprising a fiber-reinforced cement formulation and a low density additive incorporated into the formulation. The addition of the low density additive to the formulation lowers the density of the building material as compared to a building material having an equivalent fiber-reinforced cement formulation without the low density additive, while at the same time the building material with the low density additive has less than about a 20% increase in moisture expansion as compared to a building material having an equivalent fiber-reinforced cement formulation without the low density additive. More preferably, the addition of the low density additive to the formulation lowers the density of the building material as

compared to a building material having an equivalent fiber-reinforced cement formulation without the low density additive, while at the same time the low density additive either maintains or decreases the moisture expansion of the building material as compared to a building material having an equivalent fiber-reinforced cement formulation without the low density additive. The density of the building material is preferably about 1.2 g/cm<sup>3</sup> or less.

5 In another aspect of the present invention, a building material formulation is provided to form a building product. The formulation comprises a hydraulic binder, an aggregate, fibers and volcanic ash. In one embodiment, the volcanic ash improves the workability and lowers the density of the final building product by more than about 10% as compared to a building product made from an equivalent formulation without volcanic ash. In another embodiment, the formulation with volcanic ash has a negligible difference in the moisture expansion of the final product whereby the product either maintains or increases moisture expansion by less than about 20% as compared to a building product made from an equivalent formulation without volcanic ash. For the degree of density modification achieved, this moisture movement increase is surprisingly low. With nominally the same formulation ingredients, it has been found that the differences in moisture expansion for volcanic ash formulations exist. Such differences are primarily due to fluctuations in the surface area of raw materials.

10 In another aspect of the present invention, a method of forming a low density building material is provided. Hydraulic binder, aggregate, volcanic ash and water are mixed to create a slurry. The slurry is processed into a green shaped article. The green shaped article is cured to form the low density building material. In one embodiment, the article is cured by autoclaving. In another embodiment, the low density building material formed has a density of about 1.2 g/cm<sup>3</sup> or less, and a moisture expansion of about 0.17% or less.

15 In another aspect of the present invention, a building material formulation comprises a hydraulic binder, an aggregate, fibers and hollow ceramic microspheres. The final building material has a density of about 1.2 g/cm<sup>3</sup> or less. In one embodiment, about 4.1%-15% cellulose fibers are provided in the formulation. In one preferred embodiment, the microspheres lower the density of the final building product by more than about 15%, even more preferably more than about 30%, as compared to a building product made from an equivalent formulation without microspheres. In another embodiment, the microspheres decrease the moisture expansion of the final product as compared to a building product made from an equivalent formulation without microspheres, preferably by more than about 5%, more preferably by more than about 10%. In one preferred embodiment, a combination of microspheres with other additional low density additives such as volcanic ash and/or low bulk density CSH are provided in the formulation.

20 In another aspect of the present invention, a method of forming a low density building material, comprising mixing hydraulic binder, aggregate, fibers, hollow ceramic microspheres and water to create a slurry. The slurry is processed into a green shaped article. The green shaped article is cured to form the low density building material. The resulting building material has a density of about 1.2 g/cm<sup>3</sup> or less. In one embodiment, more than about 4% fibers are mixed to create the slurry. In another embodiment, the article is cured by autoclaving.

25 Brief Description of the Drawings

30

FIGURE 1 is a graph of MIP pore size distribution for a Hatschek manufactured board with and without hollow ceramic microspheres after freeze-thaw testing.

FIGURE 2 is a graph of BET pore size distribution for a Hatschek manufactured board with and without hollow ceramic microspheres after freeze-thaw testing.

5        FIGURE 3 is an SEM photograph illustrating a Hatschek manufactured board with 10 wt.% hollow ceramic microspheres showing no degradation after 147 freeze-thaw cycles.

FIGURE 4 is a graph illustrating the relationship between low density additive addition, density and strength.

#### Detailed Description of the Preferred Embodiments

10        The preferred embodiments of the present invention describe a fiber-reinforced cement building material incorporating at least one of two low density additives, hollow ceramic microspheres and/or volcanic ash. It will be appreciated that these additives may be used not only for the types of building materials described herein (i.e., fiber-reinforced materials), but may be used for other building materials as well. In addition, various combinations of microspheres and/or volcanic ash with other density modifiers are also contemplated to lower the density and improve the overall performance of the building material. Furthermore, other low density additives similar to hollow ceramic  
15        microspheres and volcanic ash that achieve the properties of lowering density while maintaining or decreasing moisture expansion of the final product, as well as improving workability, durability and other properties (as discussed below), are also contemplated as being within the scope of this invention.

#### 1.        First Embodiment - Volcanic Ash

20        In a first embodiment, this invention relates to the addition of volcanic ash into cementitious cellulose fiber reinforced building materials. Volcanic ash is also commonly referred to as "airborne perlite", "pumice" or "pumicite". Volcanic ash is typically a natural glass derived from the magma of volcanoes during an eruption. Volcanic ash is a relatively lightweight sand sediment formed by the cooling of high temperature magma, giving rise to a material comprising about 30 wt.% crystalline minerals and 70 wt.% amorphous volcanic ash glass. It has a typical bulk density of about 25-75 lbs./cu.ft. Usually this volcanic ash is expanded with the introduction of heat to change the  
25        morphology and achieve a lighter material with a typical bulk density ranging from about 2-25 lbs./cu.ft. Expanded volcanic ash can have a wide range of particle sizes from less than about 10 microns up to about 425 microns, with median particles sizes ranging between about 20 to 100 microns. The chemical composition primarily consists of silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), and potassium oxides ( $\text{K}_2\text{O}$ ).

30        Volcanic ash or expanded volcanic ash is available through suppliers such as Tufflite Inc. of Phoenix, AZ; California Industrial Minerals of Friant, CA; US Pumice of Chatsworth, CA; Amcor Precast of Idaho Falls, ID; Hess Pumice Products of Malad City, ID; Kansas Minerals Inc. of Mankato, KS; Calvert Corporation of Norton, KS; Copar Pumice Company of Espanola, NM; C.R. Minerals of Santa Fe, NM; Utility Block of Albuquerque NM; and Cascade Pumice of Bend, OR.

35        One preferred formulation of the first embodiment of the present invention comprises a hydraulic binder, aggregate, fiber, volcanic ash and additives. The hydraulic binder is preferably Portland cement but can also be, but is

not limited to, high alumina cement, lime, ground granulated blast furnace slag cement and gypsum plasters or mixtures thereof. The aggregate is preferably ground silica sand but can also be, but is not limited to, amorphous silica, diatomaceous earth, rice hull ash, blast furnace slag, granulated slag, steel slag, mineral oxides, mineral hydroxides, clays, magnesite or dolomite, polymeric beads, metal oxides and hydroxides, or mixtures thereof. The fiber is preferably cellulose wood pulp but can also be, but is not limited to, ceramic fiber, glass fiber, mineral wool, steel fiber, and synthetic polymer fibers such as polyamides, polyester, polypropylene, polymethylpentene, polyacrylonitrile, polyacrylamide, viscose, nylon, PVC, PVA, rayon, glass ceramic, carbon or any mixtures thereof. The additives can include, but are not limited to, silica fume, geothermal silica, fire retardant, thickeners, pigments, colorants, plasticisers, dispersants, foaming agents, flocculating agents, water-proofing agents, organic density modifiers, aluminum powder, kaolin, alumina trihydrate, mica, metakaolin, calcium carbonate, wollastonite, polymeric resin emulsions, or mixtures thereof.

Volcanic ash can be used in a variety of building products all having different proportions of hydraulic binder, aggregate, volcanic ash and additives to obtain optimal properties for a particular application (e.g., siding, roofing, trim, soffit, backerboard for tile underlay, etc.). It will be appreciated that the percentage of volcanic ash may be varied depending on the desired application. One preferred composition may include about 5%-80% Portland cement, about 0%-80% silica, about 4.1%-15% cellulose, about 0%-10% additives and about 2%-50% volcanic ash. One particular example of a typical formulation with volcanic ash is as follows:

Portland Cement (binder)	28%
Silica (aggregate)	54%
Cellulose (fiber)	7%
Metal Hydroxide (additive)	4%
Volcanic Ash (LDA)	7%.

Preferably, the cement and silica have a fineness index of about 200 to 450 m<sup>2</sup>/kg. The fineness index for both cement and silica is tested in accordance with ASTM C204-96a.

The material may be formed into a green shaped article from a waterborne mixture or slurry by a number of conventional processes as would be known to one of skill in the art, such as the:

- Hatschek sheet process;
- Mazza pipe process;
- Magnani process;
- Injection molding;
- Extrusion;
- Hand lay-up;
- Molding;
- Casting;
- Filter pressing;

- Flow on machine, roll forming, etc.

with or without post pressing. The processing steps and parameters used to achieve the final product using a Hatschek process are described in Australian Patent No. 515151.

The material is preferably pre-cured for up to 80 hours, most preferably 24 hours or less, to establish the formulation to set. The material is then air-cured (approximately 28 days) or more preferably, autoclaved at an elevated temperature and pressure in a steam saturated environment at 120 to 180°C for 3 to 30 hours, most preferably 24 hours or less. The length and time chosen for curing is dependent on the formulation, the manufacturing process, and the form of the article.

### Test Results

#### Density & Workability

The addition of volcanic ash in fiber cement materials lowers density and improves overall workability properties at an economical price while reducing the moisture expansion observed with that of typical low density additives. Products with volcanic ash are lighter, and therefore easier to handle, nail, and score and snap to the desired dimensions. Formulations with volcanic ash also reduce edge cracking or crumbling (if any) when the board is nailed close to the edge (e.g., 3/8-3/4"). Tables 1 and 2 below illustrate FRC formulations and test results for these formulations, more particularly demonstrating the advantages of adding volcanic ash to lower density and improve workability.

**Table 1- Formulations for Table 2 Test Results**

Formula Identification	Portland Cement	Silica	Cellulose	Metal Hydroxide	Expanded Volcanic Ash
	Hydraulic Binder	Aggregate	Fiber	Additive	LDA
B	28.7	60.3	7.0	4.0	
K	28.7	52.8	7.0	4.0	7.5

**Table 2- Comparison of Properties With and Without Volcanic Ash**

Test Method	Formulation K <sup>1</sup> 7.5% Volcanic Ash	Formulation B: Control No LDA
O.D. Density (g/cm <sup>3</sup> )	1.11	1.34
Nail Penetration <sup>3</sup> (Equilibrium conditions) <sup>2</sup> mm. of nail in material 50 mm (2 in.) - length of nail	45.4	33.0
Standard Deviation	1.1	1.0

<sup>1</sup> 7.5 wt. % of the aggregate from the control, Formulation B, has been displaced by 7.5% Volcanic Ash for Formulation K.



<sup>2</sup> Equilibrium conditions - samples are conditioned in a controlled atmosphere of  $73 \pm 4^\circ\text{F}$  and  $50 \pm 5\%$  humidity. Refer to text below for definition and description of nail penetration test.

<sup>3</sup> Refer to text below for definition and description of nail penetration test.

5 Table 2 above compares test results of 10" x 10" filter pressed prototype boards with and without volcanic ash. Prototype boards are produced by mixing the desired formulation with a Hobart Mixer to form a homogenous slurry. The slurry is then compressed between two steel dewatering plates at 3500 psi for one minute with a Wabash Press (model # PC-75-4TM) to form a monolithic sheet. The slurry is supported with steel wire mesh screens (30 to 10 40 US mesh) placed underneath and on top of the slurry mix within the steel frame mold. The monolithic sheet is then pre-cured for a minimum of about 12 hours and autoclaved at an elevated temperature and pressure in a steam saturated environment at  $150^\circ\text{C}$  for about 12 hours.

In Table 2, Formulation K with 7.5 wt.% volcanic ash lowers the density by about 17% from  $1.34\text{ g/cm}^3$  to  $1.11\text{ g/cm}^3$  when compared to an equivalent formulation, Formulation B, the control formulation without volcanic ash. 15 An equivalent formulation is herein defined as one in which the preferred LDA (e.g., volcanic ash) is displaced by an equivalent percentage of binder, aggregate and/or additives, and more preferably is displaced by an equivalent percentage of aggregate. This lowered density also improves the nailability, or ease of driving a nail into the board. Testing showed an increase in nail penetration from 33.0 mm to 45.4 mm, where 50 mm represents the length of the nail and therefore the maximum nail penetration attainable. Nail penetration testing consists of nailing a layered stack 20 of board using a Paslode Impulse<sup>®</sup> cordless framing hardware gun (positive placement) to ensure consistent nailing pressure. The layered stack typically comprises  $\frac{1}{4}$  -  $\frac{1}{2}$ " thick board stacked to a height greater than the length of the nail (2 in. or 50 mm). Senco 6d galvanized clipped head nails (part #GC21AABN) were used.

Thus, in one embodiment, as compared to a typical building sheet having a density of about  $1.3\text{ g/cm}^3$ , the building material formulation described above results in a final product having a density of less than about  $1.2\text{ g/cm}^3$ . 25 More preferably, the addition of volcanic ash to the building material formulation can preferably be adjusted to give a final product density of about  $1.2\text{ g/cm}^3$  or less, or about a 10% or more reduction in density as compared to an equivalent formulation without volcanic ash. It is further contemplated that larger additions of volcanic ash will further lower the density of the building product.

#### Wet-Dry Dimensional Stability

30 Cured fiber cement formulations with conventional density modifiers have increased moisture expansion and increased moisture absorption on a percentage weight increase basis compared to FRC formulations with no LDA. One advantage of the first embodiment over prior art is that the addition of volcanic ash attains the desired density and workability with less moisture expansion than other conventional low density additives when introduced on a similar weight percent basis. Wet-dry dimensional stability is desired in building products for quality and durability of the 35 installed product, especially in exterior applications subject to severe climatic changes. Good dimensional stability minimizes any gaps that may open between sheets or lengths of building panel or plank. Good dimensional stability

also reduces the likelihood of sheet cracking due to developed stress between the dimensionally changing panel or plank and the supporting framework that the product is fastened.

Tables 3 and 4 below illustrate FRC formulations and test results for these formulations, more particularly demonstrating the advantages of adding volcanic ash to lower density while minimizing moisture expansion typical of other low density additives added on an equivalent weight basis.

Table 3- Formulations for Table 4 Test Results

Formula Identification	Portland Cement	Silica	Cellulose	Metal Hydroxide	Expanded Volcanic Ash	Expanded Perlite
	Hydraulic Binder	Aggregate	Fiber	Additive	LDA	LDA
B	28.7	60.3	7.0	4.0		
K	28.7	52.8	7.0	4.0	7.5	
L	28.7	55.3	7.0	4.0		5.0

Table 4- Moisture Expansion<sup>1</sup> Comparison of Volcanic Ash & Perlite.

Formulation	Description	O.D. Density (g/cm <sup>3</sup> )	Moisture Expansion %	% Moisture Expansion Increase from Control
B <sup>2</sup>	Control- No LDA	1.33	0.18 ± 0.02	
K <sup>3</sup>	7.5% VA	1.11	0.17 ± 0.02	-5.5
L	5% Perlite	1.22	0.22 ± 0.02	22.2

<sup>1</sup> Moisture expansion is the change in product length from saturated to oven dry conditions. The % change moisture expansion equation is:

$$\frac{Length_{initial} - Length_{final}}{Length_{final}} \times 100.$$

<sup>2</sup> Throughout this description of the preferred embodiments Formulation B is used for the control. However, as no one sample incorporating Formulation B is used for all of the tests, nominal differences may be found in the test results for any one sample.

<sup>3</sup> 7.5 wt. % of the aggregate from the control, Formulation B, has been displaced by 7.5% Volcanic Ash for Formulation K.

Table 4 above displays test results of 10" x 10" filter-pressed prototype boards comparing formulations with 7.5 wt.% volcanic ash and 5.0% perlite (Harborlite 2000 from Harborlite Corp.), a typical low density additive. Formulation L with 5.0% perlite has a 22.2% increase in moisture expansion from the control whereas Formulation K with 7.5% volcanic ash actually shows a decrease of more than about 5% in moisture expansion from the control.

Thus, the addition of volcanic ash provides better dimensional stability than typical density modifiers at equivalent or lower weight percent additions. This allows volcanic ash to achieve lower densities and better workability properties with equivalent or higher additions of volcanic ash relative to conventional low density additives.

More preferably, the addition of volcanic ash can be adjusted to show a negligible difference in moisture expansion as compared to an equivalent formulation without volcanic ash. In one embodiment, the volcanic ash preferably will increase the moisture expansion of the final product by less than about 20% compared to a building product formed from an equivalent formulation without volcanic ash, and will more preferably decrease the moisture expansion of the final product. In one preferred embodiment, the moisture expansion of a building product made from a formulation having volcanic ash is about 0.17% or less.

## 2. Second Embodiment - Hollow Ceramic Microspheres

A second embodiment of this invention encompasses the addition of hollow ceramic microspheres into cementitious cellulose fiber-reinforced building materials. This second embodiment with hollow ceramic microspheres may be preferred over the first embodiment including volcanic ash because the addition of microspheres in FRC materials has even better moisture resistance coupled with other durability advantages, including freeze-thaw resistance, and thermal dimensional stability. It will be appreciated that the preferred embodiments for the second embodiment are not limited to these types of microspheres or building materials. Thus, other types of fillers and building materials are also contemplated.

Microspheres can be natural, synthetic or a by-product. The material can be crystalline but is more typically amorphous or glass. One preferred type of microspheres are hollow ceramic microspheres commonly known as cenospheres. Cenospheres are a coal ash by-product that is typically separated from fly ash by a floatation process where the spheres float to the surface of water from clarifiers, ponds or lakes. The microspheres are available, for example, under the names Extendspheres®, Recyclospheres® and Zeeospheres®, and are available from suppliers such as PQ Corporation of Chattanooga, Tennessee; Zeelan Industries Inc./3M of St. Paul, Minnesota; Sphere Service, Inc. of Oak Ridge, Tennessee; and Advanced Cement Technologies (A.C.T.) of Blaine, Washington.

The microspheres have typical particle sizes ranging from about 12 to 300 microns, with median particle sizes ranging about 80 to 120 microns. These sizes can, of course, vary between samples. The preferred microspheres typically contain about 62-65% silica ( $\text{SiO}_2$ ), about 23-26% alumina ( $\text{Al}_2\text{O}_3$ ) and about 3.0 to 4.0% iron oxides ( $\text{Fe}_2\text{O}_3$ ). When introduced into a building material, the microspheres introduce pores in the material that may not readily fill with water, which is advantageous to the material because of a lower saturated mass, improved wet to dry dimensional stability and improved freeze-thaw resistance.

One preferred formulation of the second embodiment comprises a hydraulic binder, aggregate, fiber, hollow ceramic microspheres and additives. It will be appreciated that the various components of the preferred formulation for the second embodiment can include any of the aforementioned materials listed for each component in the first embodiment. The material may also be produced by a number of conventional processes and curing conditions as listed and described in the first embodiment. If applicable, the preferences of the raw materials, processes, steps or conditions are similar to that of the first embodiment.

The microspheres can be used in a variety of building products all having different proportions of hydraulic binder, aggregate, microspheres and additives to obtain optimal properties for a particular application (e.g., siding,

roofing, trim, soffit, backerboard for tile underlay, etc.). One preferred composition may include about 5%-80% Portland cement, about 0%-80% silica, about 4.1%-15% cellulose, about 0%-10% additives and about 2%-90% microspheres. One particular example of a typical formulation with microspheres is as follows:

Portland Cement (binder)	28.7%
Silica (aggregate)	50.3%
Cellulose (fiber)	7%
Metal Hydroxide (additive)	4%
Microspheres (LDA)	10%.

It will be appreciated that the percentage of microspheres may be varied depending on the desired application. For instance, high addition percentages (up to about 90 wt.%) of microspheres may be suitable for building materials and systems that require some type of fire resistance rating. The high addition of microspheres provides the material with low thermal shrinkage.

#### Test Results

##### Density

Lowering the density with microspheres improves the overall workability of thicker products without compromising the advantages fiber cement products offer with regard to durability (i.e., dimensional stability) and structural integrity. These attributes are particularly advantageous for product thicknesses above about three eighths of an inch ( $> 3/8"$ ). The products with microspheres are lighter and therefore easier to handle. Secondly, products with microspheres are easier to nail and score / snap to the desired dimension. Furthermore, microsphere formulations reduce edge cracking or crumbling (if any) when the board is nailed close to the edge (e.g.,  $3/8$ - $5/8"$ ).

Tables 5 and 6 below display formulations and test results for FRC formulations, more particularly illustrating the advantages of adding microspheres to a formulation to improve density and workability.

**Table 5- Formulations for Table 6 Test Results**

Formula Identification	Portland Cement	Silica	Cellulose	Metal Hydroxide	Microspheres
	Hydraulic Binder	Aggregate	Fiber	Additive	LDA
B	28.7	60.3	7.0	4.0	
A	28.7	50.3	7.0	4.0	10.0

Table 6 - Comparison of Properties With and Without Microspheres

Test Method	Formulation A <sup>1</sup> 10% Microspheres	Formulation B Control No LDA
Density (Equilibrium Conditions) <sup>2</sup> (g/cm <sup>3</sup> )	1.16	1.39
Nail Penetration (Equilibrium conditions) mm. of nail in material 50 mm (2 in.) = length of nail standard deviation	47.0 0.9	31.7 1.4

<sup>1</sup> 10% microspheres in Formulation A replace 10% of the aggregate in the control, Formulation B.

<sup>2</sup> Equilibrium conditions- samples are conditioned in a controlled atmosphere of 73±4°F and 50±5% humidity.

Table 6 displays test results of 3' x 5' Hatschek manufactured board for Formulations A and B. Formulation A with 10 wt.% microspheres reduces the density by about 15% from 1.39 g/cm<sup>3</sup> to 1.16 g/cm<sup>3</sup> when compared to an equivalent formulation without microspheres (Formulation B). In addition, the ease of driving a nail into the board is improved. Testing revealed an increase in nail penetration from 31.7 mm to 47.0 mm, where 50 mm represents the length of the nail and the maximum nail penetration attainable.

Overall, testing of prototypes and products produced from trials has revealed about a 15% decrease in density for every 10% addition of microspheres and significant improvements in nailing. Thus, the addition of microspheres may advantageously be used to reduce the density of FRC building material by more than about 15%, even more preferably more than about 30%, as compared to an equivalent formulation without microspheres. The present inventors contemplate that with the addition of microspheres, the density of the material can be reduced to about 0.9 g/cm<sup>3</sup> (see Table 10 below), and more preferably, even as low as about 0.5 g/cm<sup>3</sup>.

#### Wet-Dry Dimensional Stability

As stated earlier, cured fiber cement formulations with conventional density modifiers have increased moisture expansion and increased moisture absorption on a percentage weight increase basis. One advantage of the preferred embodiments over prior art is that the addition of microspheres to reduce density does not increase moisture expansion from wet to dry. This is useful for a number of reasons previously mentioned in the first embodiment.

Table 7 below displays test results of 3' x 5' Hatschek manufactured board with and without microspheres. Formulation A with 10% microspheres maintains, or more preferably reduces moisture expansion from that of Formulation B without microspheres. Formulations A and B are in Table 5 above.

Table 7 - Comparison of Moisture Expansion With and Without Microspheres

Test Method	Formulation A <sup>1</sup> 10% Microspheres	Formulation B Control No LDA
Density (Equilibrium Conditions) <sup>2</sup> (g/cm <sup>3</sup> )	1.16	1.39
Moisture Expansion % Change	0.15 ± 0.02	0.16 ± 0.02

<sup>1</sup> 10% microspheres in Formulation A replace 10% of the aggregate in the control, Formulation B.

<sup>2</sup> Equilibrium conditions - samples are conditioned in a controlled atmosphere of 73±4°F and 50±5% humidity.

Tables 8-10 below display formulations and test results for 10" x 10" filter pressed prototype boards comparing microspheres with conventional density modifiers that do increase moisture expansion. Conventional density modifiers include low bulk density calcium silicate hydrate (CSH), and expanded polystyrene, vermiculite, perlite, shale or clay.

Table 8 - Formulations for Tables 9 and 10 Test Results

Formula Identification	Portland Cement	Silica	Cellulose	Metal Hydroxide	Micro-spheres	Low Bulk Density CSH	Expanded Perlite
	Hydraulic Binder	Aggregate	Fiber	Additive	LDA	LDA	LDA
B	28.7	60.3	7.0	4.0			
C	35.2	52.8	8.0	4.0			
D	26.8	40.2	8.0		25.0		
E	26.8	40.2	8.0				25.0
F	28.7	55.3	7.0	4.0		5.0	

Table 9 data below displays a conventional low density additive, low bulk density CSH (Silasorb from Celite Corp.), at a 5% load that increases moisture expansion from that of the control, Formulation B.

Table 9 - Moisture Expansion of Low Bulk Density CSH

Formula Identification	Description	Equilibrium Density <sup>1</sup> (g/cm <sup>3</sup> )	Moisture Expansion %
B	Control	1.41	0.162 ± 0.02
F <sup>2</sup>	5.0% low bulk density CSH	1.27	0.188 ± 0.02

<sup>1</sup> Equilibrium conditions- samples are conditioned in a controlled atmosphere of 73±4°F and 50±5% humidity

<sup>2</sup> 5% low bulk density CSH in Formulation F replaces 5% of the aggregate in the control, Formulation B.

Table 10 below compares two formulations with the same base formula, one with 25 wt.% microspheres and the other with 25 wt.% perlite (Aztec XX from Aztec Perlite). Both the perlite and microsphere formulations decrease the density of control Formulation C from 1.3 g/cm<sup>3</sup> to around 0.9 g/cm<sup>3</sup>, but moisture expansion increases with the perlite formulation and decreases with the microsphere formulation.

**Table 10- Moisture Expansion Comparison of Microspheres & Perlite.**

Formulation	Description	equilibrium Density <sup>1</sup> (g/cm <sup>3</sup> )	Moisture Expansion %
C	Control	1.31	0.230 ± 0.02
D	25% Microspheres	0.90	0.202 ± 0.02
E	25% Perlite	0.89	0.275 ± 0.02

<sup>1</sup> Equilibrium conditions- samples are conditioned in a controlled atmosphere of 73±4°F and 50±5% humidity

<sup>2</sup> For formulations D and E, microspheres displace both the aggregate and hydraulic binder in the control, formulation C.

Thus, the addition of microspheres to the fiber cement formulation has the effect of maintaining or reducing moisture expansion of the final product. Preferably, the addition of microspheres can be adjusted to reduce the moisture expansion by about 5%, more preferably by about 10% or more, as compared to a similar formulation without microspheres.

#### Freeze-Thaw Resistance

Freeze-thaw resistance refers to a material's resistance to damage when exposed to repeated cycles of freezing and thawing. For instance, concrete can be damaged by frost, and especially by repeated cycles of freezing and thawing. Damage usually begins with flaking at the surface, and gradually extends inward, though deep cracks may occur. Damage associated with freezing generally does not occur unless a sufficient quantity of water is present in the pores, and is minimal in dense concrete of low water-to-cement ratio and low permeability.

Similar to high density concrete, freeze-thaw damage is minimal in high-density fiber cement. In the preferred embodiments, the addition of microspheres into a FRC formulation produces a lower density cured product that maintains freeze-thaw resistance, unlike prior art where density modifiers added to the formulation reduce a material's freeze-thaw resistance.

**FIGURES 1** and **2** display pore size distribution graphs of 3' x 5' Hatschek manufactured board using MIP (mercury intrusion porosimetry) and BET (Brunauer, Emmett and Teller) methods. There is less change in pore size distribution for Formulation A with 10 wt.% microspheres after 147 freeze-thaw cycles than Formulation B without microspheres after 126 cycles. This demonstrates the microsphere formulation's resistance to structural change typical of freeze-thaw damage. To further support the microsphere formulation's resistance to freeze-thaw damage, **FIGURE 3** displays a SEM (scanning electron microscope) picture of a Hatschek manufactured board (3' x 5') with 10 wt. % microspheres showing no signs of degradation after 147 freeze-thaw cycles whereas other wood cement composites would typically have degradation at this stage.

Freeze-thaw testing of **FIGURE 3** was performed in accordance with ASTM (American Standard Test Method) C666A titled "Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing." This test method has two different procedures, A or B. Procedure A was followed, meaning samples were submerged in water for both rapid freezing and thawing as opposed to rapid freezing in air and rapid thawing in water (procedure B). Samples are periodically removed from freeze-thaw cycling and visually inspected for degradation such as cracking, moisture expansion, sponginess/wetting throughout the sample, and overall structural integrity. Samples are moved from freeze-thaw cycling when the degree of degradation is such that the sample does not hold together and would therefore not be functional as a building product.

#### High Temperature Dimensional Stability

Reducing a building material's thermal shrinkage prevents high temperature stresses and strains from occurring on building components. This improved thermal- dimensional stability allows building components in building fires to maintain a shield to fire without cracking, falling apart and allowing fire to spread quickly.

Tables 11 and 12 below display FRC formulations and test results for 10" x 10" filter-pressed prototype boards, more particularly illustrating the advantages of adding microspheres to a formulation to improve high temperature dimensional stability.

**Table 11- Formulations for Table 12 Test Results**

Formula Identification	Portland Cement	Silica	Cellulose	Metal Hydroxide	Micro-spheres	Low Bulk Density CSH
	Hydraulic Binder	Aggregate	Fiber	Additive	LDA	LDA
A	28.7	50.3	7.0	4.0	10.0	
B	28.7	60.3	7.0	4.0		
F	28.7	55.3	7.0	4.0		5.0
G	28.7	50.3	7.0	4.0		10.0
H	28.7	40.3	7.0	4.0	20.00	

**Table 12-  
Thermal Shrinkage Comparison of Microspheres & Low Bulk Density CSH**

Formulation	Description	Equilibrium Density <sup>2</sup> (g/cm <sup>3</sup> )	Thermal Shrinkage <sup>1</sup> (%)
B	Control	1.41	3.07
F <sup>3</sup>	5.0% low bulk density CSH	1.21	7.27
G <sup>3</sup>	10.0% low bulk density CSH	1.15	8.09
A <sup>3</sup>	10.0% microspheres	1.15	4.41
H <sup>3</sup>	20.0% microspheres	1.01	4.21

<sup>1</sup> Refer to text below for description of thermal shrinkage test.

<sup>2</sup> Equilibrium conditions- samples are conditioned in a controlled atmosphere of 73±4°F and 50±5% humidity.

<sup>3</sup> The percent LDA in formulations F, G, A & H replace an equivalent percent of



aggregate in the control, Formulation B.

At lower load levels (e.g., about 10-20%), microspheres minimize the high temperature thermal shrinkage that occurs when typical inorganic density modifiers are introduced in fiber-cement formulations. Table 12 displays results of the percent thermal shrinkage obtained for Formulation A with 10 wt.% microspheres versus Formulation G with 10 wt.% low bulk density CSH (Silasorb from Celite Corp.). Compared to the control (Formulation B), both formulations reduce density from about 1.4 to 1.15 g/cm<sup>3</sup>, but the formulation with low bulk density CSH has almost twice the thermal shrinkage as the formulation with microspheres. Moreover, Formulation H with 20.0 wt.% microspheres and a density of about 1.0 g/cm<sup>3</sup> has over 40% less thermal shrinkage than Formulation F with only 5.0% low bulk density CSH (Silasorb from Celite Corp.) and a higher density of about 1.2 g/cm<sup>3</sup>.

High temperature thermal shrinkages were determined using a Thermomechanical Analyzer (TMA). Samples were cut to 10 by 25 mm with up to 12 mm thickness. The temperature of the saturated samples was ramped up at a rate of 20° C/minute to 950° C and sample dimensions were measured with a macroexpansion probe. Thermal shrinkage was taken as the overall dimensional change from 25° to 950° C, and reported as a percentage of total initial length.

Another advantage of using microspheres in fiber-cement formulations is thermal shrinkage decreases as microsphere additions increase. Thermal shrinkage with microspheres is inversely proportional to the weight percent added, whereas thermal shrinkage with conventional density modifiers is directly proportional to the weight percent added. Thus, formulations with higher additions of microspheres (up to about 90 wt.%) have lower thermal shrinkage than formulations with lower additions (up to about 20 wt.%).

Table 13 below provides formulations with high additions of microspheres and Table 14 provides the high temperature thermal shrinkage results. Formulations I and J with 70 and 90 wt.% microsphere additions produce thermal shrinkage results of about 2.7 and 1.1%, respectively. Thermal shrinkage for Formulations I and J were determined by cutting samples approximately 10 x 10 x 40 mm long, oven drying, firing for one hour at 1000° C with a muffle furnace, and allowing to cool to oven dry conditions. The percent thermal shrinkage was determined by measuring the overall difference in length from oven dry to 1000° C, and dividing by the initial oven dry length.

Table 13- Formulations For Table 14 Results

Formula Identification	Portland Cement	Silica Fume	Cellulose	Microspheres
	Hydraulic Binder	Aggregate	Fiber	LDA
I	26.2	2.9	0.9	70.0
J	8.7	1.0	0.3	90.0

Table 14- Thermal Shrinkage of High-Addition Microsphere Formulations

Formula Identification	Thermal Shrinkage%
I	2.7
J	1.1

Thus, in an embodiment where 20% microspheres are used in the fiber cement formulation, the thermal shrinkage of the final product as compared to an equivalent product made from a formulation without microspheres increases by less than about 50%. As described above, with increasing percentages of microspheres, the percent thermal shrinkage decreases, even to a point where, as compared to a product without microspheres, the final product with microspheres exhibits a lower thermal shrinkage, preferably lower from about 10% to about 70%. More particularly, the thermal shrinkage of the product with microspheres is preferably less than about 4%.

### 3. Third Embodiment - Microspheres and Other Additives

A third embodiment of this invention relates to the addition of hollow ceramic microspheres in combination with volcanic ash and/or other low density additives in cementitious cellulose fiber-reinforced building materials. Descriptions of volcanic ash and hollow ceramic microspheres are found in the detailed descriptions of the first and second embodiments, respectively. The third embodiment with a blend of microspheres and low density additives may be more preferable than the first embodiment with VA given FRC products can achieve a lower range of densities with improved moisture resistance and durability properties. However, the second embodiment with the independent addition of microspheres may be preferable to this third embodiment because of the superlative durability properties offered by the independent addition of microspheres. The preference of the second embodiment to the third embodiment is dependent on the relative importance of durability in a particular application.

Similar to the first and second embodiments, one preferred formulation of the third embodiment comprises of a hydraulic binder, aggregate, fiber, hollow ceramic microspheres, low density additives and other additives. It will be appreciated that the various components of the third embodiment can include any of the aforementioned materials listed for each component in the first embodiment. The third embodiment may also be produced by a number of conventional processes and curing conditions as listed and described in the first embodiment. If applicable, the preferences of the raw materials, processes, steps or conditions are similar to that of the first embodiment.

The blending of microspheres with VA and/or low density additives can be used in a variety of building products all having different proportions of hydraulic binder, aggregate, low density additives, and other additives to obtain optimal properties for the particular application (e.g., siding, roofing, trim, soffit, backerboard for tile underlay, etc.). One preferred composition of the third embodiment could include about 5-80% Portland cement, about 0%-80% silica, about 4.1%-15% cellulose, about 0%-10% additives and about 2%-60% microspheres and other typical LDA. One particular example of a typical formulation with a blend of microspheres and a typical low density additive is as follows:

Portland Cement (binder)	28.7%
Silica (aggregate)	50.3%
Cellulose (fiber)	7%
Metal Hydroxide (additive)	4%
Microspheres (LDA)	10%
Volcanic Ash (LDA)	5%

It will be appreciated that the percentage of microspheres and other LDA's including VA may be varied depending on the desired application.

#### Test Results

##### Lower Densities with Durability

There are several advantages to blending microspheres with VA or other typical low density modifiers such as low bulk density CSH, or expanded polystyrene beads, clay, vermiculite, perlite, and shale. One advantage is that an equivalent or lower density can be achieved with less total weight percent addition (than microspheres only) given the lower densities of VA and other typical LDA compared to microspheres. The lower addition rates with the blend are more economical, and the microspheres minimize moisture expansion associated with the addition of typical inorganic density modifiers. Another advantage to blending microspheres with other typical low density additives is that FRC products can achieve lower density ranges and still maintain sufficient product strength for handling. Thus, higher load levels (on a percent weight basis) of the combination of microspheres and other LDA can be added while minimizing the adverse effects typical low density additives have on dimensional stability and overall durability.

The addition of low density additives in all of the embodiments described herein is not the only means of reducing density in cement based formulations, however. Formulations consisting of cement and aggregate without fiber or low density additives have densities typically ranging from about 1.8- 2.1 g/cm<sup>3</sup>. Adding fiber to cement formulations is advantageous because fiber also lowers density in addition to providing strength and products suitable for nailing. Densities for fiber cement formulations with greater than about 4 wt.% fiber typically range from about 1.2 to 1.4 g/cm<sup>3</sup>. It has been found that FRC formulations with about 4 wt.% or less fiber do not have sufficient strength and ductility for installation. These FRC products are often too brittle and nailing produces cracks or blowouts during installation. Alternatively, fiber additions greater than about 15 wt.% may in some applications be undesirable because fiber in FRC formulations contributes to moisture expansion, increased permeability, and overall compromises in durability.

Thus, the right balance of fiber must be advantageously determined for a FRC product, which is dependent on the thickness and shape of the particular product. In one embodiment, fiber percentages of about 4.1% to 15% are preferable. Low density additives are added to FRC formulations to provide additional reductions in density from that of the fiber addition. However, in general, the higher the addition of LDA, the lower the strength properties of the FRC product. Therefore, LDA additions are limited because FRC products should preferably maintain a minimum strength for sufficient handling and installation. The maximum LDA addition is dependent on a multitude of factors such as the

Table 17 below displays test results of 10" x 10" filter-pressed prototype boards with four formulations containing variances primarily only in additions of various low density additives, and a control without any low density additives. Results show that Formulation M with 12 wt.% microspheres reduces density from that of the control from 1.35 g/cm<sup>3</sup> to 1.16 g/cm<sup>3</sup>, but Formulation N with 11 wt.% addition of the microspheres/low bulk density CSH (Silasorb from Celite) blend lowers the density further to 1.10 g/cm<sup>3</sup>. Moreover, moisture expansion for Formulation N with the 11 wt.% microspheres/low bulk density CSH blend and the control without low density additives is not significantly different at 0.167 and 0.163%, respectively. In comparison, Formulation G with only 10 wt.% low bulk density CSH provides about the same density as Formulation N's 11 wt.% blend, but with a notably higher moisture expansion of 0.197%. The subtle wt.% differences of hydraulic binder and aggregate in the formulations do not have an impact on density or moisture expansion properties.

Table 17 - Moisture Expansion Comparisons

Formula Identification	Description	O.D. Density (g/cm <sup>3</sup> )	Moisture Expansion %
B	Control -No LDA	1.35	0.163 ± 0.02
M	12% Microspheres	1.16	0.156 ± 0.02
N	6% Microspheres 5% Low Bulk Density CSH	1.10	0.167 ± 0.02
G	10% Low Bulk Density CSH	1.12	0.197 ± 0.02

<sup>1</sup> The percent LDA in Formulations M, N and G primarily replace the aggregate in the control with no LDA, Formulation B.

### Conclusions

In general, it will be appreciated that the preferred embodiments of the present invention, more particularly, a fiber-reinforced building material containing additives of volcanic ash, hollow ceramic microspheres, or a combination of microspheres, volcanic ash and/or other additives, have several advantages over the prior art. These materials have a low density compared to conventional fiber cement building products. This enables production of a thicker product (e.g., 3/8" to 1.0") that is lighter and therefore easier to handle, cut, nail and install.

The materials also have improved wet-dry dimensional stability and the building material's durability is improved such that building panels do not excessively shrink and crack. Also, excessive gaps between panels or planks do not open up after changes in humidity or from wet to dry seasons.

With respect to at least the formulations and building products incorporating hollow ceramic microspheres, the materials' freeze-thaw resistance is maintained at lower density, unlike most inorganic density modified fiber cement materials. This gives these materials good durability in climates that experience frequent freezing and thawing conditions.

These materials incorporating microspheres also have improved fire resistance properties because of improved thermal dimensional stability relative to typical low density additives. Thus, the materials are stable in building fires as

a building component such that the material can maintain a shield to fire without cracking and falling apart and allowing fire to spread quickly.

5 The preferred embodiments have applicability to a number of building product applications, including but not limited to building panels (interior and exterior), tile backer board (walls and floors), siding, soffit, trim, roofing, fencing and decking. The embodiments illustrated and described above are provided merely as examples of certain preferred embodiments of the present invention. Various changes and modifications can be made from the embodiments presented herein by those skilled in the art without departure from the spirit and scope of the invention.

WHAT IS CLAIMED IS:

1. A building material, comprising:  
a fiber-reinforced cement formulation; and  
a low density additive incorporated into the formulation, wherein the low density additive lowers  
5 the density of the building material as compared to a building material having an equivalent fiber-reinforced  
cement formulation without the low density additive, while at the same time the building material with the  
low density additive has less than about a 20% increase in moisture expansion as compared to a building  
material having an equivalent fiber-reinforced cement formulation without the low density additive;  
wherein the density of the building material is about 1.2 g/cm<sup>3</sup> or less.
- 10 2. The building material of Claim 1, wherein the density of the building material is about 0.5 to 1.2  
g/cm<sup>3</sup>.
3. The building material of Claim 1, wherein the density of the building material is about 0.9 to 1.1  
g/cm<sup>3</sup>.
4. The building material of Claim 1, wherein the low density additive substantially maintains or  
15 decreases the moisture expansion of the building material as compared to a building material having an equivalent fiber-  
reinforced cement formulation without the low density additive.
5. The building material of Claim 1, wherein the median particle size of the low density additive is  
between about 20 and 120  $\mu$ m.
6. The building material of Claim 1, wherein the low density additive is volcanic ash.
- 20 7. The building material of Claim 6, wherein the formulation incorporates about 2-50% volcanic ash.
8. The building material of Claim 1, wherein the low density additive comprises hollow ceramic  
microspheres.
9. The building material of Claim 8, wherein the formulation incorporates about 2-90% hollow ceramic  
microspheres.
- 25 10. The building material of Claim 8, wherein the formulation further incorporates a second low density  
additive in addition to the hollow ceramic microspheres.
11. The building material of Claim 10, wherein the second low density additive is volcanic ash.
12. The building material of Claim 10, wherein the second low density additive is calcium silicate  
hydrate.
- 30 13. The building material of Claim 12, wherein the formulation incorporates up to about 30% low bulk  
density calcium silicate hydrate.
14. The building material of Claim 1, wherein the formulation incorporates greater than about 4%  
fibers.
15. The building material of Claim 14, wherein the formulation incorporates cellulose fibers.
- 35 16. A building material formulation used to form a building product, comprising:

35. The method of Claim 30, wherein the low density building material has a density of about 1.2 g/cm<sup>3</sup> or less.

36. The method of Claim 30, wherein the moisture expansion of the low density building material is about 0.17% or less.

5 37. The method of Claim 30, wherein the article is cured by autoclaving.

38. A building material formulation used to form a building product, comprising:  
a hydraulic binder;  
an aggregate;  
fibers; and  
10 hollow ceramic microspheres;  
wherein the final building material has a density of about 1.2 g/cm<sup>3</sup> or less.

39. The formulation of Claim 38, wherein the hydraulic binder is Portland cement.

40. The formulation of Claim 39, comprising about 5 to 80% Portland cement.

41. The formulation of Claim 38, wherein the aggregate comprises silica.

15 42. The formulation of Claim 41, comprising about 0-80% silica.

43. The formulation of Claim 38, further comprising about 0-10% additives.

44. The formulation of Claim 38, wherein the fiber is cellulose wood pulp

45. The formulation of Claim 44, comprising about 4.1-15% cellulose.

46. The formulation of Claim 38, wherein the microspheres are cenospheres.

20 47. The formulation of Claim 38, comprising about 5-30% microspheres.

48. The formulation of Claim 38, comprising up to about 90% microspheres.

49. The formulation of Claim 38, wherein the microspheres lower the density of the final building product by more than about 15% as compared to a building product made from an equivalent formulation without microspheres.

25 50. The formulation of Claim 38, wherein the microspheres lower the density of the final building product by more than about 30% as compared to a building product made from an equivalent formulation without microspheres.

51. The formulation of Claim 38, wherein the microspheres substantially maintain the moisture expansion of the final product as compared to a building product made from an equivalent formulation without microspheres.

30 52. The formulation of Claim 38, wherein the microspheres decrease the moisture expansion of the final product as compared to a building product made from an equivalent formulation without microspheres by more than about 5%.

53. The formulation of Claim 52, wherein the microspheres decrease the moisture expansion of the final product as compared to a building product made from an equivalent formulation without microspheres by more than about 10%.

54. The formulation of Claim 38, wherein the microspheres increase the number of cycles that the final product begins to visually degrade under freeze-thaw cycling as compared to a building product made from an equivalent formulation without microspheres.

55. The formulation of Claim 38, wherein the microspheres decrease the change in pore size distribution in the final product after undergoing a number of freeze-thaw cycles as compared to a building product made from an equivalent formulation without microspheres.

56. The formulation of Claim 38, wherein the microspheres affect the thermal shrinkage of the final product as compared to a building product made from an equivalent formulation without microspheres such that the thermal shrinkage of the final product is less than about 50% greater than that of the building product without microspheres.

57. The formulation of Claim 38, wherein the thermal shrinkage of the final product is between about 1% and 5%.

58. The formulation of Claim 38, further comprising volcanic ash.

59. The formulation of Claim 38, further comprising low bulk density calcium silicate hydrate.

60. A method of forming a low density building material, comprising:

mixing hydraulic binder, aggregate, fibers, hollow ceramic microspheres and water to create a slurry;

processing the slurry into a green shaped article; and

curing the green shaped article to form the low density building material, the building material having a density of about 1.2 g/cm<sup>3</sup> or less.

61. The method of Claim 60, wherein the fibers are cellulose wood pulp.

62. The method of Claim 61, comprising mixing greater than about 4% of the fibers with the hydraulic binder, aggregate, hollow ceramic microspheres and water to create the slurry.

63. The method of Claim 60, further comprising mixing additives with the hydraulic binder, aggregate, fibers, hollow ceramic microspheres and water to create the slurry.

64. The method of Claim 60, further comprising mixing low density additives with the hydraulic binder, aggregate, fibers, hollow ceramic microspheres and water to create the slurry.

65. The method of Claim 64, wherein the low density additives include calcium silicate hydrate.

66. The method of Claim 60, wherein the low density building material has a density of between about 0.5 and 1.2 g/cm<sup>3</sup>.

67. The method of Claim 60, wherein the low density building material has a density of between about 0.9 and 1.1 g/cm<sup>3</sup>.



68. The method of Claim 60, wherein the article is cured by autoclaving.

1/4

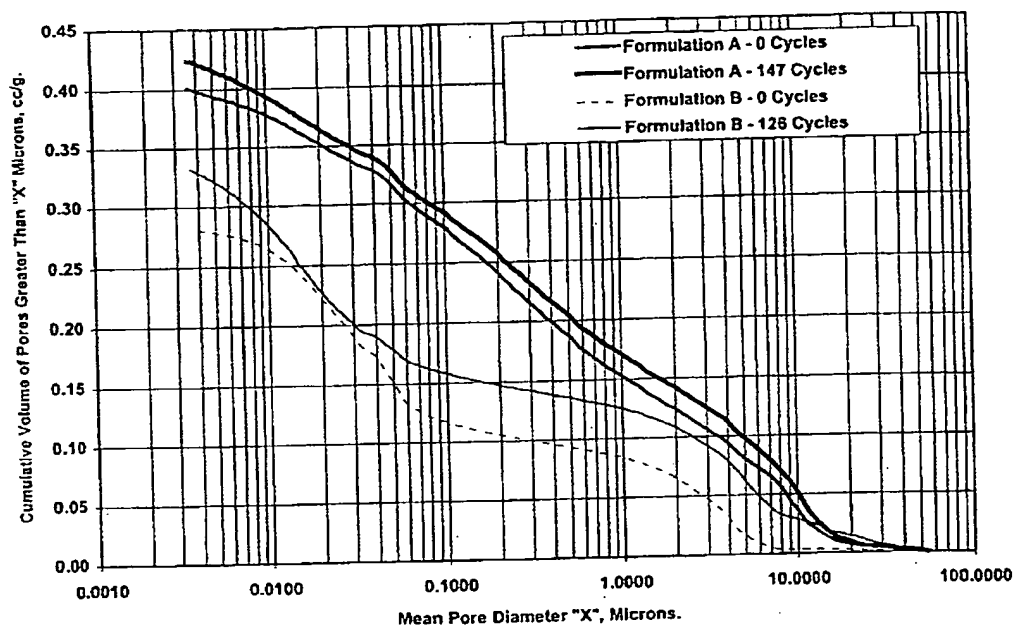


FIG. 1

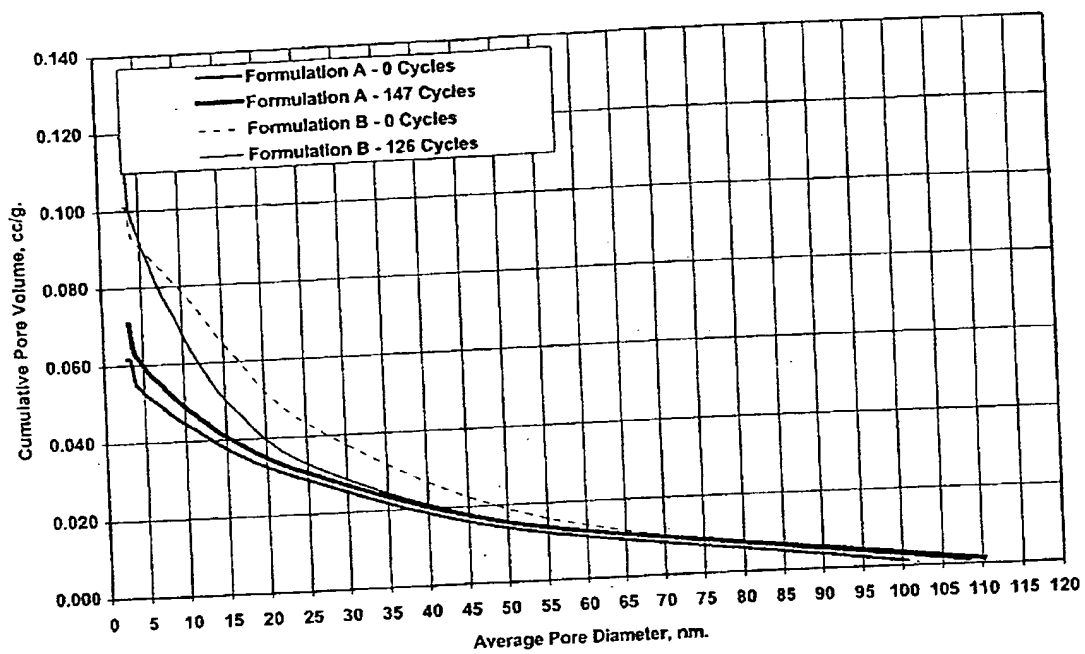
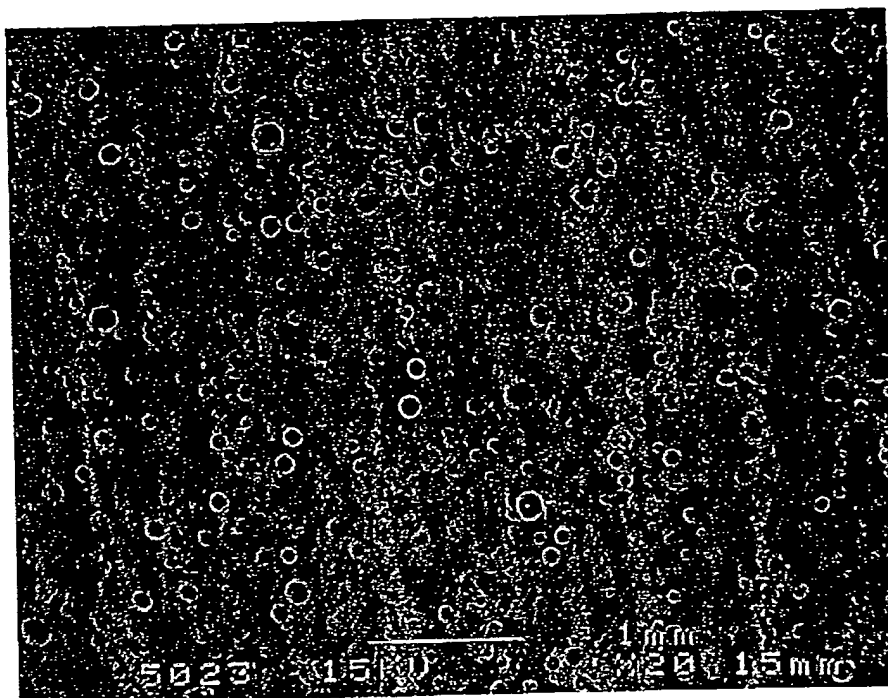


FIG. 2



F16.3

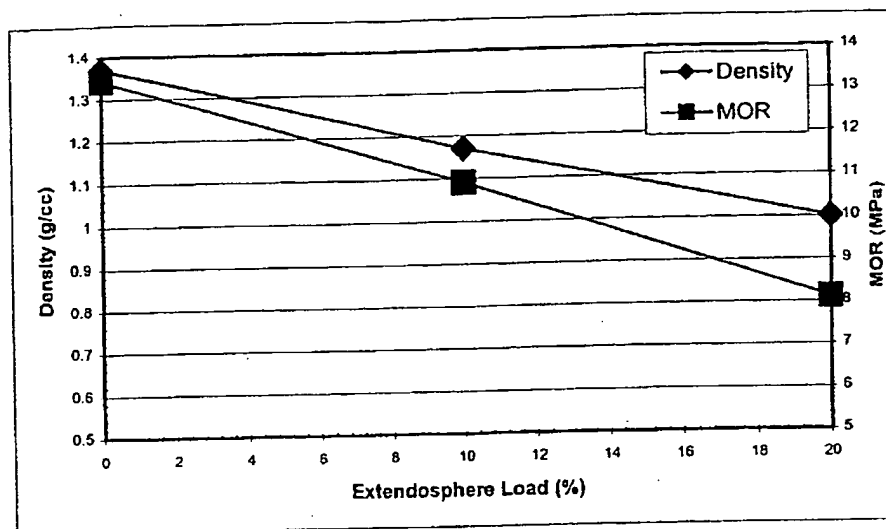


FIG. 4

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 01/07948

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C04B14/14 C04B18/08 C04B38/08 C04B28/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 00 21901 A (CHEN HONG ; KIRBY NIGEL (AU); BLACK ANDREW (AU); MONEY ERIK (AU); H) 20 April 2000 (2000-04-20)  page 9, line 30,31 page 10, line 16,17; claims 1-3,10,17,84	1-5, 8-10, 12-15, 38-57, 59-68
X	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 12, 26 December 1996 (1996-12-26) & JP 08 217561 A (CHICHIBU ONODA CEMENT CORP) abstract	1-5, 8-10,14, 15, 38-57, 60-64,68
A	DE 198 58 342 C (KALKSANDSTEIN WERK WEMDING GMB) 3 February 2000 (2000-02-03) page 3, line 7-15; claims 1,15	1,38,46, 60
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&\* document member of the same patent family

Date of the actual completion of the international search

10 August 2001

Date of mailing of the international search report

22/08/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo.nl  
Fax: (+31-70) 340-3016

Authorized officer

Daeleman, P

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/07948

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEMICAL ABSTRACTS, vol. 117, no. 6, 10 August 1992 (1992-08-10) Columbus, Ohio, US; abstract no. 54763d, H. SAKOTA, ET AL.: page 390; XP000374916 abstract & JP 04 089340 A (ID.) 23 March 1992 (1992-03-23) ---	
A	GB 2 041 384 A (PENNINGTON J) 10 September 1980 (1980-09-10) ---	
X	DATABASE WPI Week 199521 Derwent Publications Ltd., London, GB; AN 1995-155696 XP002174598 & CN 1 081 168 A (CONSTR ENG RES INST BEIJING) abstract ---	16-20, 24
P, X	DATABASE WPI Week 200059 Derwent Publications Ltd., London, GB; AN 2000-617403 XP002174599 & NO 9 901 129 A (ELKEM) abstract ---	16, 17, 19, 20, 23, 24
A	---	1, 6, 7, 30, 31, 34
X	CHEMICAL ABSTRACTS, vol. 110, no. 18, 1 May 1989 (1989-05-01) Columbus, Ohio, US; abstract no. 159518m, H. SAKOTA, ET AL.: page 340; XP000017481 abstract ---	16, 17, 19-24, 30-34
A	& JP 63 257631 A (ID.) 25 October 1988 (1988-10-25) ---	1, 6
X	CHEMICAL ABSTRACTS, vol. 114, no. 10, 11 March 1991 (1991-03-11) Columbus, Ohio, US; abstract no. 87565g, A. YADA ET AL.: page 360; XP000192004 abstract & JP 02 192447 A (ID.) 30 July 1990 (1990-07-30) ---	16, 25

-/--

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/07948

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 118, no. 14, 5 April 1993 (1993-04-05) Columbus, Ohio, US; abstract no. 130759v, F. KATAHIRA ET AL.: page 395; XP000401485 abstract & JP 04 295072 A (ID) 20 October 1992 (1992-10-20)	1,2,6, 16-25,28
A	CHEMICAL ABSTRACTS, vol. 118, no. 14, 5 April 1993 (1993-04-05) Columbus, Ohio, US; abstract no. 130760p, M. SAKAI ET AL.: page 395; XP000401486 abstract & JP 04 300232 A (ID) 23 October 1992 (1992-10-23)	



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/07948

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0021901 A	20-04-2000	AU 1137300 A	01-05-2000
JP 08217561 A	27-08-1996	NONE	
DE 19858342 C	03-02-2000	WO 0035826 A	22-06-2000
JP 04089340 A	23-03-1992	NONE	
GB 2041384 A	10-09-1980	NONE	
CN 1081168 A	26-01-1994	NONE	
NO 9901129 A		NONE	
JP 63257631 A	25-10-1988	NONE	
JP 02192447 A	30-07-1990	NONE	
JP 04295072 A	20-10-1992	JP 3024236 B	21-03-2000
JP 04300232 A	23-10-1992	NONE	